(12) EUROPEAN PATENT APPLICATION

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(54) **Polyethylene blends.**

(57) A composition of matter comprising: (a) 5 to 40 weight percent inclusive of a low molecular weight ethylene resin made using a titanium catalyst system said resin having a density greater than 0.955 grams per cubic centimeter, a melt index greater than 25 grams per 10 minutes, and a heterogeneity index between 2 and 8 inclusive; and (b) 60 to 95 weight percent inclusive of a high molecular weight ethylene copolymer resin made using a chromium catalyst system said resin having a density of at least 0.93 grams per cubic centimeter, a high load melt index between 1.5 and 15 grams per 10 minutes, and a heterogeneity index between 6 and 100 inclusive; wherein said composition of matter has a melt index greater than 0.05 grams per 10 minutes.

BACKGROUND OF THE INVENTION

This invention relates to polyethylene blends.

It is known in the art to blend components with dissimilar characteristics to achieve a blend with superior performance properties. However, this task is not easy to accomplish. For example, the components of a blend can interact antagonistically resulting in a lowering of the expected performance of the blend, or the components can interact producing a blend that is only the mere aggregation of the separate component parts.

Thermoplastic blends are very desirable for applications such as pipes, films, and bottles. However, each application requires a resin tailored for that particular application. Furthermore, each of these tailored resins are judged by many performance attributes. While it is possible to improve one attribute it is often necessary to find a compromise of the various attributes in order to find a resin which fulfills the customers requirements.

This invention provides an improved compromise of characteristics thereby increasing the availability of possible solutions to consumer demands.

SUMMARY OF THE INVENTION

It is an object of this invention to provide an improved polyethylene blend.

It is another object of this invention to provide a polyethylene blend with an improved environmental stress crack resistance.

These and other objects of this invention will become apparent to those skilled in the art from the following detailed description of the invention.

In accordance with this invention, a composition of matter is provided comprising: (a) 5 to 40 weight percent inclusive of a low molecular weight ethylene resin made using a titanium catalyst system said resin having a density greater than 0.955 grams per cubic centimeter, a melt index greater than 25 grams per 10 minutes, and a heterogeneity index between 2 and 8 inclusive; and (b) 60 to 95 weight percent inclusive of a high molecular weight ethylene copolymer resin made using a chromium catalyst system said resin having a density of at least 0.93 grams per cubic centimeter, a high load melt index between 1.5 and 15 grams per 10 minutes, and a heterogeneity index between 6 and 100 inclusive; wherein said composition of matter has a melt index greater than 0.05 grams per 10 minutes.

DETAILED DESCRIPTION OF THE INVENTION

The composition of this invention comprises two components. The first component comprises a low molecular weight polyethylene made using a titanium catalyst system. The second component comprises a high molecular weight polyethylene made using a chromium catalyst system. These two components are blended together to provide a polyethylene blend which has desirable properties. Further information concerning the characteristics of these two components is given below.

Polyethylene is a thermoplastic material available in a wide range of flow rates and densities. Polyethylene offers useful properties such as toughness at a variety of temperatures, stiffness ranging from flexible to rigid, as well as excellent chemical resistance. Currently, polyethylene can be fabricated and processed by most known thermoplastic processes in the art.

Polyethylene is generally classified primarily on the basis of two characteristics, namely, density and flow rate (commonly identified as melt index). ASTMD 1248-84 (reapproved 1989) provides a convenient system for categorizing polyethylene resins. First, polyethylene resins are generally classified according to density: type I polyethylene has a nominal density between 0.910-0.925 grams/cubic centimeter (g/cm³); type II polyethylene has a nominal density between 0.926-0.940 g/cm³; type III polyethylene has a nominal density between 0.941-0.959 g/cm³; and type IV polyethylene has a nominal density of 0.960 g/cm³ or above. Type I polyethylene is usually defined as a low density resin. Type II polyethylene is usually classified as a medium density resin. Type III and IV polyethylene resins are usually classified as high density resins.

Within each density type there exists five different categories of flow rates. A category 1 polyethylene resin has a nominal flow rate greater than 25 g/10 min. at a temperature of 190°C and under a 2160 gram weight load. A category 2 polyethylene resin has a nominal flow rate greater than 10 and up to and including 25 g/10 min. A category 3 polyethylene resin has a nominal flow rate greater than 1 up to and including 10 g/10 min. A category 4 polyethylene resin has a nominal flow rate greater than 0.4 up to an including 1.0 g/10 min. A category 5 polyethylene resin has a nominal flow rate equal to or less than 0.4

g/10 min.

These types and categories of polyethylene resin can be made by various processes known in the art. For example, types I and II polyethylene can be made by a high pressure process which uses oxygen, peroxide and/or other strong oxidizers as a catalyst. Pressures of reaction ranging from 100 to 350 MPa are typically employed. Polyethylene resins formed in these types of processes are highly branched with short side chains occurring every 15 to 40 carbon atoms on the chain backbone. Furthermore, the crystallinity of these types of polyethylene resins is approximately 40 to 60 percent with the amorphous content of the polymer increasing as the density is reduced.

On the other hand, types I, II, III, and IV polyethylene can be produced from such processes as slurry, solution, or gas phase processes. These processes are generally known as low pressure processes. Catalysts used in these processes vary widely, but the most frequently used are transition metals in combination with metal halides or activated metal oxides. Reaction pressures normally fall within 0.25 MPa to 6 MPa. The polyethylene produced by these processes is more linear in nature, that is, little or no long chain branching occurs. Linear polyethylene of types I and II is approximately 50 percent crystalline and types III and IV can be as high as 85 percent crystallinity or more. Generally, polyethylenes made by a low pressure process which have a density below 0.960 are made by polymerizing ethylene with a small amount of comonomer such as propylene, 1-butene and/or 1-hexene.

Low Molecular Weight Polyethylene Resin

The low molecular weight polyethylene resin must be produced from a titanium catalyst system. Exemplary titanium catalyst systems are broadly disclosed in U.S. Patents 4,394,291; 4,236,988; and 4,347,158; which are hereby incorporated by reference.

The low molecular weight polyethylene resin can be any new or recycled ethylene resin. Generally, the characteristics of the low molecular weight polyethylene resin are those listed below in Table I.

Table I

Low Molecular Weight Polyethylene Resin Characteristics			
Characteristic	Broad Range	Preferred Range	Most Preferred Range
Density[1]	$D \geq 0.955$	$D \geq 0.96$	$0.96 \leq D \leq 0.98$
Heterogeneity Index[2]	$2 \leq H.I. \leq 8$	$2 \leq H.I. \leq 7$	$2 \leq H.I. \leq 6$
Melt Index[3]	$MI > 25$	$30 \leq M.I. \leq 1500$	$75 \leq M.I. \leq 1000$
Weight Percent[4]	$5 \leq W.P. \leq 40$	$8 \leq W.P. \leq 35$	$10 \leq W.P. \leq 33$

[1]Density is in grams per cubic centimeter.

[2]The Heterogeneity Index is a measure of the molecular weight distribution. This is a valuable indicator of a resin's usefulness in certain applications. It is the weight average molecular weight divided by the number average molecular weight.

[3]Melt Index is in grams per 10 minutes at FR-190/2.16.

[4]The Weight Percent is based on the total weight of both the low molecular weight polyethylene resin and the high molecular weight polyethylene resin.

The low molecular weight polyethylene resin generally has a very low environmental stress crack resistance (ESCR).

High Molecular Weight Polyethylene Resin

The high molecular weight polyethylene resin must be produced from a chromium catalyst system. Exemplary chromium catalyst systems are broadly disclosed in U.S. Patents 3,887,494; 3,900,457; 3,947,433; 4,053,436; 4,151,122; 4,294,724; 4,364,839; 4,364,841; 4,364,841; 4,392,990; and 4,405,501; which are hereby incorporated by reference.

The high molecular weight polyethylene resin can be any new or recycled ethylene copolymer resin. The comonomer used to produce the copolymer is generally an alpha-olefin with about 3 to about 20 carbon atoms per molecule. Preferably, the comonomer has from about 3 to about 10 carbon atoms per molecule and most preferably from about 3 to about 8 carbon atoms per molecule. Examples of alpha-olefins useful in this invention as comonomers are propylene, 1-butene, 3-methyl-1-butene, 1-pentene, 3-

methyl-1-pentene, 4-methyl-1-pentene, 1-hexene, 3-ethyl-1-hexene and 1-octene. The amount of comonomer incorporated will generally comprise less than about 40 weight percent of the high molecular weight resin. Preferably, the high molecular weight polyethylene resin will comprise from about 0.0001 to about 30 weight percent comonomer, and most preferably will comprise from about 0.01 to about 15 weight percent comonomer. Generally, the characteristics of the high molecular weight polyethylene resin are those listed below in Table II.

Table II

High Molecular Weight Polyethylene Resin Characteristics			
Characteristic	Broad Range	Preferred Range	Most Preferred Range
Density[1] Heterogeneity Index[2] High Load Melt Index[3] Weight Percent[4]	$D \geq 0.93$ $6 \leq H.I. \leq 100$ $1.5 < H.L.M.I. < 15$ $60 \leq W.P. \leq 95$	$0.94 \leq D \leq 0.975$ $6 \leq H.I. \leq 75$ $2 \leq H.L.M.I. < 12$ $65 \leq W.P. \leq 92$	$0.95 \leq D \leq 0.965$ $6 \leq H.I. \leq 50$ $2 \leq H.L.M.I. \leq 10$ $67 \leq W.P. \leq 90$

[1] See footnote 1 Table I.
[2] See footnote 2 Table I.
[3] The High Load Melt Index is in grams per 10 minutes at FR 190/21.60.
[4] See footnote 4 Table I.

The high molecular weight polymer resin generally has a very high ESCR. Usually the ESCR of these polymers are so high that they cannot be practically measured.

Blending of Components

The blending of the components can be accomplished by any method known in the art which produces a homogeneous blend from two polymer resins. Standard polymer processing equipment can be used to make these blends such as, for example, single screw extruders, twin screw extruders, and continuous mixers. Additionally, during blending, other components can be added to the blend. These components can be antioxidants, UV stabilizers, preservatives, and processing aids such as fluoroelastomers. After blending it is important that the resin be easy to process. Generally, this means that the melt index of the polymer blend needs to be greater than 0.05 grams per 10 minutes. Preferably, the melt index of the blend is from 0.1 to 5 grams per 10 minutes $(0.1 \leq M.I. \leq 5)$.

EXAMPLE

This example is provided to further assist a person skilled in the art with understanding this invention. The particular reactants, conditions, and the like, are intended to be generally illustrative of this invention and are not meant to be construed as unduly limiting the reasonable scope of this invention.

The following test methods were used to determine the properties of the polyethylene samples.

(1) The density was determined in accordance with ASTMD 1505-85. This is a standard test method for determining the density of plastics. The density is reported in grams per cubic centimeter $(D = g/cm^3)$.

(2) The flow rate was determined in accordance with ASTMD 1238-65T. This is a standard test method for determining the flow rate of a thermoplastic. Two different conditions were used to determine the flow rate. Condition 1 consisted of a temperature of 190°C and a total load of 2.16 kilograms (FR-190/2.16) which is also called the melt index. Condition 2 consisted of a temperature of 190°C and a total load weight of 21.60 kilograms (FR-190/21.60) which is also called the high load melt index.

(3) The environmental stress crack resistance was determined in accordance with ASTMD 1693-70. This is a standard test method for determining the environmental stress cracking resistance of ethylene plastics. The test specimens were prepared by the following procedure ASTMD 1928-80 Procedure C. The condition that the test was run at was condition A. The ESCR is reported in hours.

(4) The heterogeneity index (Mw/Mn), which is the weight average molecular weight (Mw) divided by the number average molecular weight (Mn), was determined using data collected by gel permeation chromatography. This gel permeation chromatography was accomplished with a Waters 150C chromatograph at 140°C with 1,2,4-trichlorobenzene as a solvent. This is a standard test method for determining weight and number average molecular weights and molecular weight distributions.

Blend Preparation

The low molecular weight polyethylene resins and the high molecular weight polyethylene resins were stabilized with 0.05 weight percent of BHT (butylated hydroxytoluene), 0.03 weight percent of DLTDP (dilauryl thiodipropionate), and 0.04 weight percent calcium stearate based on the total weight of the resin. These two polyethylene resins were premixed in a container by agitation then they were placed in a mixer for more complete blending. In general, the blending was conducted in a Midget Banbury mixer at a temperature between 150°C to 160°C for approximately 5 minutes at a mixing speed of 130 rpm and any large pieces were then ground in a mill.

Table E1

Low Molecular Weight Polyethylene Resin			
Number	Melt Index	Density	Mw/Mn
L1	304	0.9686	3.7

Table E2

High Molecular Weight Polyethylene Resin			
Number	Melt Index	Density	Mw/Mn
H1	1.6 HLMI	0.9604	21.4
H2	2.4 HLMI	0.9599	22.9

Table E3

Polyethylene Blend					
Number	Composition	Melt Index	HLMI	Density	ESCR
B1	33%L1+67%H1	0.20	70	0.9665	165 (Condition A)
B2	22%L1+78%H2	0.14	38	0.9599	>1000 (Condition A)

Table E4

Comparison Polymers			
Number	Melt Index	Density	ESCR
C1	0.3	0.949	500
C2	0.35	0.952	50
C3	0.35	0.957	45
C4	1.0	0.957	30
C5	0.75	0.964	15-20

The comparison polymers are all polyethylenes resins. They are all made from chromium catalyst systems except for HHN 5710 which was made from a titanium catalyst system. They can be obtained from the Phillips Petroleum Company as HHM 4903, HHM 5202, HHM 5502, HHN 5710, and EHM 6007, respectively.

Comparing the polyethylene blends of Table E3 with the Comparison Polymers of Table E4 it is apparent that blends B1 and B2 have a superior ESCR to all of the Comparison Polymers where the melt index and density are comparable. The only Comparison Polymer which has an ESCR greater than 50 also

has a much lower density of 0.949g/cm³. The densities of the inventive blends are significantly higher than Comparison Polymer C1's density.

Claims

1. A composition of matter comprising:
   (a) 5 to 40 weight percent of a low molecular weight ethylene resin made using a titanium catalyst system said resin having a density greater than 0.955 grams per cubic centimeter, a melt index greater than 25 grams per 10 minutes, and a heterogeneity index in the range of 2 and 8; and
   (b) 60 to 95 weight percent of a high molecular weight ethylene copolymer resin made using a chromium catalyst system said resin having a density of at least 0.93 grams per cubic centimeter, a high load melt index in the range of 1.5 and 15 grams per 10 minutes, and a heterogeneity index in the range of 6 and 100;

   wherein said composition of matter has a melt index greater than 0.05 grams per 10 minutes.

2. A composition of matter according to claim 1 wherein said copolymer comprises ethylene and a comonomer selected from the group consisting of propylene, 1-butene, 3-methyl-1-butene, 1-pentene, 3-methyl-1-pentene, 4-methyl-1-pentene, 1-hexene, 3-ethyl-1-hexene, 1-octene, or mixtures thereof.

3. A composition of matter comprising:
   (a) 10 to 33 weight percent of a low molecular weight ethylene resin made using a titanium catalyst system said resin having a density in the range of 0.96 and 0.98 g/cm³, a melt index in the range of 75 and 1,000 g/10 min., and a heterogeneity index in the range of 2 and 6; and
   (b) 67 to 90 weight percent of a high molecular weight ethylene copolymer resin made using a chromium catalyst system said resin having a density in the range of 0.95 and 0.965 g/cm³, a high load melt index in the range of 2 and 10 g/10 min., and a heterogeneity index in the range of 6 and 50;

   wherein said composition of matter has a melt index greater than 0.05 g/10 min.

4. A composition of matter according to claim 3 wherein said copolymer is a copolymer of ethylene and a comonomer selected from the group consisting of propylene, 1-butene, 3-methyl-1-butene, 1-pentene, 3-methyl-1-pentene, 4-methyl-1-pentene, 1-hexene, 3-ethyl-1-hexene, 1-octene, or mixtures thereof.

5. An article produced with a composition of matter according to one of the preceding claims, wherein said article is a film, a bottle or a pipe.

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	EP-A-0 129 312 (ASAHI KASEI KOGIO KABUSHIKI KAISHA) * page 5, paragraph 3 - page 10, paragraph 3; claims *	1-5	C08L23/04
A	EP-A-0 100 843 (PHILLIPS PETROLEUM COMPANY) * page 4, line 1 - page 6, line 2; claims *	1-5	

			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C08L

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	25 NOVEMBER 1992	CLEMENTE GARCIA R.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
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